

# PATENT COOPERATION TREATY

# PCT

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## INTERNATIONAL PRELIMINARY REPORT ON PATENTABILITY

(Chapter II of the Patent Cooperation Treaty)

(PCT Article 36 and Rule 70)

Applicant's or agent's file reference 63556A	<b>FOR FURTHER ACTION</b> See Form PCT/IPEA/416	
International application No. PCT/US2004/026275	International filing date (day/month/year) 13.08.2004	Priority date (day/month/year) 13.08.2003
International Patent Classification (IPC) or national classification and IPC C08J5/12, C09J11/06, C09J4/00, C09J4/06		
Applicant DOW GLOBAL TECHNOLOGIES INC. et al.		
1. This report is the international preliminary examination report, established by this International Preliminary Examining Authority under Article 35 and transmitted to the applicant according to Article 36. 2. This REPORT consists of a total of 5 sheets, including this cover sheet. 3. This report is also accompanied by ANNEXES, comprising: a. <input checked="" type="checkbox"/> <i>(sent to the applicant and to the International Bureau)</i> a total of 7 sheets, as follows: <input checked="" type="checkbox"/> sheets of the description, claims and/or drawings which have been amended and are the basis of this report and/or sheets containing rectifications authorized by this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions). <input type="checkbox"/> sheets which supersede earlier sheets, but which this Authority considers contain an amendment that goes beyond the disclosure in the international application as filed, as indicated in item 4 of Box No. I and the Supplemental Box. b. <input type="checkbox"/> <i>(sent to the International Bureau only)</i> a total of (indicate type and number of electronic carrier(s)) , containing a sequence listing and/or tables related thereto, in computer readable form only, as indicated in the Supplemental Box Relating to Sequence Listing (see Section 802 of the Administrative Instructions).  4. This report contains indications relating to the following items: <input checked="" type="checkbox"/> Box No. I Basis of the opinion <input type="checkbox"/> Box No. II Priority <input type="checkbox"/> Box No. III Non-establishment of opinion with regard to novelty, inventive step and industrial applicability <input type="checkbox"/> Box No. IV Lack of unity of invention <input checked="" type="checkbox"/> Box No. V Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement <input type="checkbox"/> Box No. VI Certain documents cited <input type="checkbox"/> Box No. VII Certain defects in the international application <input type="checkbox"/> Box No. VIII Certain observations on the international application		
Date of submission of the demand  10.06.2005	Date of completion of this report  28.09.2005	
Name and mailing address of the International preliminary examining authority:   European Patent Office D-80298 Munich Tel. +49 89 2399 - 0 Tx: 523656 epmu d Fax: +49 89 2399 - 4465	Authorized Officer  Otegui Rebollo, J Telephone No. +49 89 2399-8670	



**INTERNATIONAL PRELIMINARY REPORT  
ON PATENTABILITY**

International application No.  
PCT/US2004/026275

**Box No. I Basis of the report**

1. With regard to the **language**, this report is based on the international application in the language in which it was filed, unless otherwise indicated under this item.
  - This report is based on translations from the original language into the following language, which is the language of a translation furnished for the purposes of:
    - international search (under Rules 12.3 and 23.1(b))
    - publication of the international application (under Rule 12.4)
    - international preliminary examination (under Rules 55.2 and/or 55.3)
2. With regard to the **elements\*** of the international application, this report is based on (*replacement sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to this report*):

**Description, Pages**

1-18 as originally filed

**Claims, Numbers**

1-25 received on 13.06.2005 with letter of 10.06.2005

- a sequence listing and/or any related table(s) - see Supplemental Box Relating to Sequence Listing

3.  The amendments have resulted in the cancellation of:
  - the description, pages
  - the claims, Nos.
  - the drawings, sheets/figs
  - the sequence listing (*specify*):
  - any table(s) related to sequence listing (*specify*):
4.  This report has been established as if (some of) the amendments annexed to this report and listed below had not been made, since they have been considered to go beyond the disclosure as filed, as indicated in the Supplemental Box (Rule 70.2(c)).
  - the description, pages
  - the claims, Nos.
  - the drawings, sheets/figs
  - the sequence listing (*specify*):
  - any table(s) related to sequence listing (*specify*):

\* If item 4 applies, some or all of these sheets may be marked "superseded."

**INTERNATIONAL PRELIMINARY REPORT  
ON PATENTABILITY**

International application No.  
PCT/US2004/026275

**Box No. V Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement**

**1. Statement**

Novelty (N)	Yes: Claims	1-25
	No: Claims	
Inventive step (IS)	Yes: Claims	
	No: Claims	1-25
Industrial applicability (IA)	Yes: Claims	1-25
	No: Claims	

**2. Citations and explanations (Rule 70.7):**

**see separate sheet**

**INTERNATIONAL PRELIMINARY  
REPORT ON PATENTABILITY  
(SEPARATE SHEET)**

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PCT/US2004/026275

**Re Item V**

**Reasoned statement with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement**

Reference is made to the following documents:

- D1: US 2002/033227 A1 (SONNENSCHEIN MARK F ET AL) 21 March 2002(2002-03-21)
- D2: EP-A-0 405 798 (MINNESOTA MINING & MFG) 2 January 1991 (1991-01-02)
- D3: WO 03/038006 A (DOW GLOBAL TECHNOLOGIES INC ; SONNENSCHEIN MARK F (US); WEBB STEVEN P) 8 May 2003 (2003-05-08)

1. The subject-matter of claims 1 to 25 of the present application appears to lack an inventive step (Article 33(3) PCT) with respect to the known prior art for the following reasons.

1.1. D1 and D3 independently teach the use of organoborane/amine complex catalysed acrylic adhesives for joining many materials typically in sheet or membrane shape like polyolefins to structural materials such as concrete (see for instance item 67 of D1 or pages 29/30 of D3) and the good properties of the bonds produced (see for instance paragraphs 10 and 14 of D1 and its examples, or page 4, 2d and 3d paragraphs of D3 and its examples). The subject-matter of claims 1 to 10 and 12 to 25 of the application appears to derive in an obvious manner (Article 33(3) PCT) from the routine activities of the skilled person trying to use the adhesives disclosed in D1 or D3 in bonding further films, sheets or laminates, such as roofing membranes, where acrylic adhesives are usually employed (see for instance D2). Furthermore, in the photopolymerization process of D2 the actual polymerization naturally occurs by free radicals, and the initiation is not restricted to a photoinitiator but other initiators (eg those disclosed in D1 or D3) may be used therein (see page 4, lines 9 to 14, and claim 1). Note that the information given on page 4, lines 9 to 14 cannot be construed as prejudicing the use of the adhesives disclosed in D1 or D3 because claim 1 of D2 does not contain any limitation concerning the nature of the catalyst to be used with the acrylic adhesives used therein. Therefore, in view of the teachings of

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(SEPARATE SHEET)**

International application No.

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the documents above the skilled person could not have missed using, in the course of their routine activities, the organoborane/amine complex catalysed acrylic adhesives of D1 or D3 for joining roofing materials of D2.

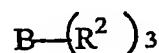
1.2. The subject-matter of claim 11 of the present application illustrates the use of silicon-substituted amines in the preparation of the organoborane/amine complexes used in the formulation of the adhesives used in documents D1 or D3, which step appears to be obvious (Article 33(3) PCT) for the skilled person as amino-silanes are widely used as adhesion improvers.

**CLAIMS:**

1. A method for joining a roofing membrane having a first surface to an object having a second surface comprising the steps of:
  - (i) applying an effective amount of a curable adhesive composition to the first surface of the roofing membrane, the second surface of the object or to both surfaces, wherein the adhesive comprises
    - (a) an effective amount of a organoborane amine complex initiator and
    - (b) one or more monomers, oligomers, polymers or mixtures thereof having olefinic unsaturation which is capable of polymerization by free radical polymerizationand
  - (ii) contacting the first surface of the roofing membrane with the second surface of the object.
2. The method of Claim 1 wherein the roofing membrane and the object independently comprise a metal, a multilayer plastic, a multilayer composite, a thermoplastic, a thermoset; or combinations thereof.
3. The method of Claim 1 wherein the roofing membrane and object are thermoplastic.
4. The method of Claim 1 wherein the roofing membrane and the object independently comprise a polyolefin; acrylonitrile, butadiene and styrene terpolymer; polyvinyl chloride; chlorinated polyvinyl chloride; chlorinated/sulfonated polyethylene; ethylene/alpha-olefin/diene terpolymers; or blends thereof.
5. The method of Claim 1 wherein the roofing membrane and the object comprise propylene polymers.
6. The method of Claim 1 wherein the roofing membrane and the object comprise ethylene polymers.

7. The method of Claim 1 wherein the roofing membrane is a first thermoplastic and the object is a second thermoplastic different from the first thermoplastic.

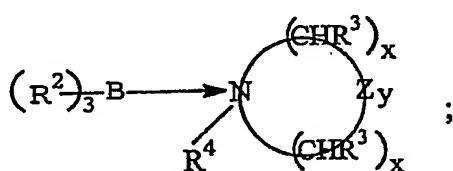
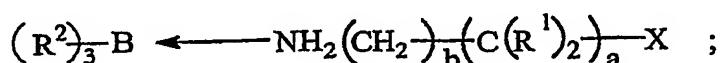
8. The method of Claim 1 wherein the organoborane amine complex includes an organoborane which has the structure

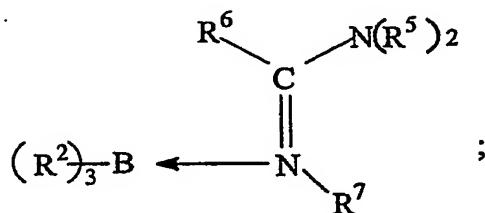
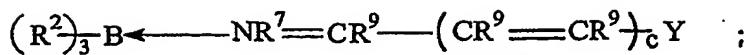


wherein B represents Boron; and R<sup>2</sup> is separately in each occurrence a C<sub>1-10</sub> alkyl, C<sub>3-10</sub> cycloalkyl, or two or more of R<sup>2</sup> may combine to form a cycloaliphatic ring.

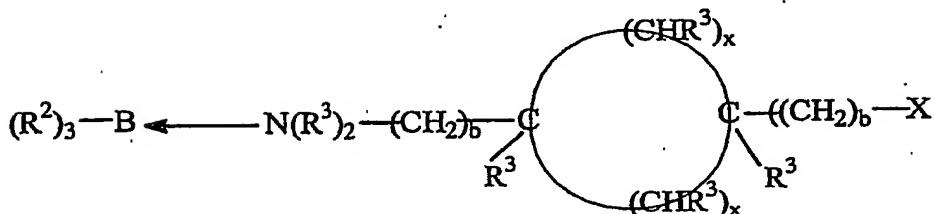
9. The method of Claim 1 wherein the organoborane amine complex includes an amine which is a primary amine; a secondary amine; a polyamine having primary or secondary amines or both; ammonia; a polyoxyalkylene amine; a reaction product of a diamine and a difunctional compound having moieties which react with an amine, wherein the reaction product has terminal amine groups; an aryl amine; a heterocyclic amine; a compound having an amidine structural component; an aliphatic heterocycle having at least one secondary nitrogen in the heterocyclic ring wherein the heterocyclic compound may also contain one or more additional secondary or tertiary nitrogen atoms, oxygen atoms, sulfur atoms, or double bonds in the heterocycle; an alicyclic compound having bound to the alicyclic ring one or more substituents containing an amine moiety; a conjugated imine or a mixture thereof.

10. The method of Claim 1 wherein the organoborane amine complex has the structure





or



wherein

B is boron;

 $R^1$  is separately in each occurrence hydrogen, a  $C_{1-10}$  alkyl or  $C_{3-10}$  cycloalkyl; $R^2$  is separately in each occurrence a  $C_{1-10}$  alkyl,  $C_{3-10}$  cycloalkyl or two or more of  $R^2$  may combine to form a cycloaliphatic ring structure; $R^3$  is separately in each occurrence hydrogen, a  $C_{1-10}$  alkyl,  $C_{3-10}$  cycloalkyl or forms a double bond with a  $R^3$  or  $R^4$  on an adjacent atom; $R^4$  is separately in each occurrence hydrogen,  $C_{1-10}$  alkyl,  $C_{3-10}$  cycloalkyl,  $C_{6-10}$  aryl or  $C_{6-10}$  alkaryl; $R^5$  and  $R^6$  are separately in each occurrence hydrogen,  $C_{1-10}$  alkyl,  $C_{3-10}$  cycloalkyl,  $N(R^4)_2$  wherein  $R^7$  is separately in each occurrence hydrogen,  $C_{1-10}$  alkyl,  $C_{3-10}$  cycloalkyl or two or more of  $R^5$ ,  $R^6$  and  $R^7$  in any combination can combine to form a ring structure which can be a single ring or a multiple ring structure and the ring structure can include one or more of nitrogen, oxygen or unsaturation in the ring structure; $R^9$  is independently in each occurrence hydrogen,  $C_{1-10}$  alkyl or  $C_{3-10}$  cycloalkyl, Y,

$-(C(R^9)_2-(CR^9=CR^9)_c-Y$  or two or more of  $R^9$  can combine to form a ring structure, or one or more of  $R^9$  can form a ring structure with  $Y$  provided the ring structure is conjugated with respect to the double bond of the imine nitrogen;

$R^{10}$  is separately in each occurrence  $C_{1-10}$  alkyl,  $C_{3-10}$  cycloalkyl or  $-(C(R^1)_2)_d-W$ ;

$W$  is separately in each occurrence hydrogen,  $C_{1-10}$  alkyl or  $X$ ;

$X$  is  $OR^{10}$ ,  $SR^{10}$  or a halogen;

$Y$  is independently in each occurrence hydrogen,  $SR^4$ ,  $N(R^4)_2$ ,  $OR^4$ ,  $C(O)OR^4$ , a halogen or an alkylene group which forms a cyclic ring with  $R^7$  or  $R^9$ ;

$Z$  is separately in each occurrence oxygen or  $-NR^4$ ;

$a$  is separately in each occurrence an integer of from about 1 to about 10;

$b$  is separately in each occurrence 0 or 1, with the proviso that the sum of  $a$  and  $b$  should be from about 2 to about 10;

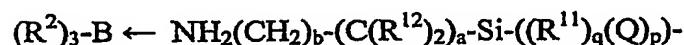
$c$  is separately in each occurrence an integer of from about 1 to about 10;

$d$  is separately in each occurrence an integer of about 1 to about 4;

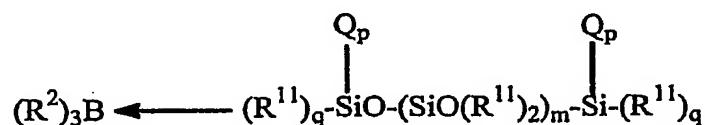
$x$  is separately in each occurrence an integer of about 1 to about 10, with the proviso that the total of all occurrences of  $x$  is from about 2 to about 10; and

$y$  is separately in each occurrence 0 or 1.

11. The method of Claim 1 where in the organoborane amine complex has the structure



or



wherein

$B$  represents Boron;

$R^2$  is separately in each occurrence  $C_{1-10}$  alkyl,  $C_{3-10}$  cycloalkyl, or two or more of  $R^2$  may combine to form a cycloaliphatic ring;  $Q$  is a hydrolyzable moiety;  $R^{11}$  is independently in each occurrence hydrogen, alkyl, alkoxy, alkenyl, alkyl amino or corresponds to the formula  $((CR^{14}H)_rO)_n-(NR^4)-(CH_2)_o-NH_2$  with the proviso that at least  $(R^{11})'$  is a primary amine leave this as is;  $R^{12}$  is independently in each occurrence hydrogen, alkyl, aryl, alkoxy, and may further contain one or more primary, secondary or tertiary amines;  $R^{14}$  is separately in each occurrence hydrogen or alkyl;  $R^4$  is hydrogen,  $C_{1-10}$  alkyl,  $C_{6-10}$  aryl or  $C_{7-10}$  alkaryl;  $a$  is a number of form 1 to 10;  $b$  is a number of from 0 to 1;  $m$  is separately in each occurrence a whole number of 1 or greater;  $p$  is separately in each occurrence a number of from 1 to 3;  $q$  is separately in each occurrence an integer from 1 to 2 wherein the sum of  $p$  and  $q$  on each silicon atom is 3;  $n$  is separately in each occurrence an integer of about 4 to about 400;  $o$  is separately in each occurrence an integer of about 1 to about 9; and  $r$  is separately in each occurrence an integer of 2 or 4.

12. The method of Claim 1 wherein the adhesive further comprises: an effective amount of an isocyanate containing compound; one or more unpolymerized or partially polymerized compound having ring opening heterocyclic moieties and optionally a Lewis acid catalyst capable of initiating polymerization of the compound containing heterocyclic moieties; one or more compound, oligomer or prepolymer having siloxane groups and reactive moieties in its backbone capable of polymerization; one or more compound, oligomer or prepolymer having siloxane groups in its backbone which contain a moiety which when exposed to moisture forms an acid capable of decomplexing the organoborane amine complex; or mixtures thereof.

13. The method of Claim 1 wherein the adhesive comprises a polymerizable acrylate monomer.
14. The method of Claim 1 wherein the adhesive has a VOC emission of less than about 650 g/l.
15. The method of Claim 1 wherein the adhesive has a VOC emission of less than about 270 g/l.
16. A method to repair a new or existing roofing membrane, object, or roofing membrane/object joint having one or more surface in need of repair comprising the steps of
  - (i) applying an effective amount of a curable adhesive composition to the surface(s) in need of repair, a repair patch or both the surface in need of repair and the repair patch, wherein the adhesive comprises
    - (a) an effective amount of a organoborane amine complex initiator and
    - (b) one or more monomers, oligomers, polymers or mixtures thereof having olefinic unsaturation which is capable of polymerization by free radical polymerization.and
  - (ii) bonding a repair patch to the surface in need of repair.
17. The method of claim 1 wherein the adhesive further comprises a liquid.
18. The method of claim 18 wherein the liquid comprises water.
19. A roofing membrane having a first surface bonded to an object having a second surface, wherein the bond comprises:
  - (i) an effective amount of a curable one or two part adhesive composition to the first surface of the roofing membrane, the second surface of the object or to both surfaces, wherein the adhesive comprises
    - (a) an effective amount of a organoborane amine complex initiator and

(b) one or more monomers, oligomers, polymers or mixtures thereof having olefinic unsaturation which is capable of polymerization by free radical polymerization.

20. The method of claim 1 further comprising the step of applying an effective amount of pressure to the roofing membrane /adhesive/object in order for the adhesive to cure.

21. The method of claim 1 further comprising the step of exposing the adhesive to air for a sufficient amount of time to develop green strength of the adhesive prior to step (ii).

22. The method of Claim 1 wherein the curable adhesive compound is a one part compound.

23. The method of Claim 1 wherein the curable adhesive compound is a two part compound.

24. The method of claim 1, further comprising the step of ensuring that the first and second surfaces contain substantially no water prior to step (i).

25. The method of claim 1, further comprising the step of ensuring that the first and second surfaces are substantially oil-free prior to step (i).